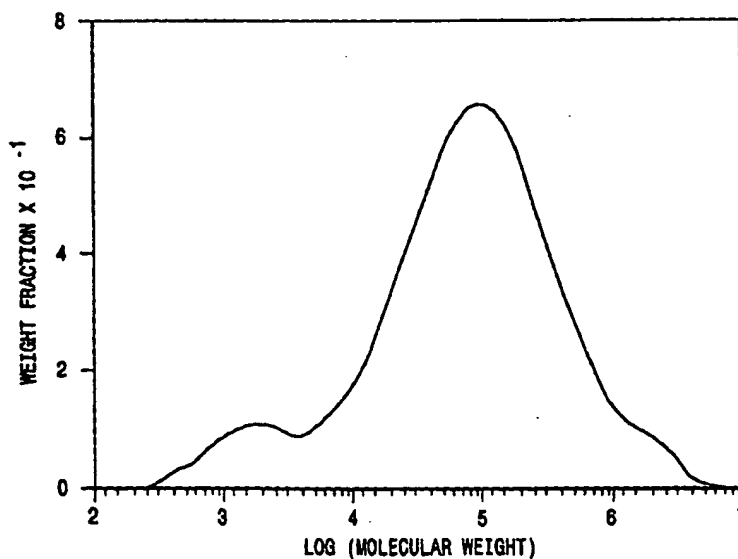




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(54) Title: ZIEGLER-NATTA CATALYST FOR ETHYLENE POLYMERIZATION OR COPOLYMERIZATION

**(57) Abstract**

A catalyst for polymerizing or copolymerizing ethylene is made by reacting silica having surface hydroxyl groups with a dialkylmagnesium compound in a hydrocarbon slurry, reacting that product with carbon tetrachloride, reacting that product with titanium tetrachloride, then reacting that product with dimethylaluminum chloride. The polymer made using this catalyst has a bimodal or trimodal molecular weight distribution, an MFR value of 28 to 70, and is produced in a single reactor. The product comprises at least two components of differing average molecular weights.

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ZIEGLER-NATTA CATALYST FOR ETHYLENE POLYMERIZATION OR COPOLYMERIZATION

This application is a continuation-in-part of copending Serial No. 08/121,821 filed September 15, 1993, which, in turn, was a continuation-in-part of application Serial No. 08/008,854 filed January 5, 1993, each of which is relied upon
5 and expressly incorporated by reference herein.

The invention relates to catalysts for the manufacture of linear polyethylene resins with densities between 0.918 and 0.945 g/cc and with a relatively narrow molecular weight distribution (MWD). Such resins can be processed on high-
10 stalk extrusion equipment at high rates with excellent bubble stability and produce film with much improved toughness relative to the film made of polyethylene resins with a relatively broad MWD.

The present invention relates to a method for
15 copolymerizing ethylene and alpha-olefins, a catalyst for such a copolymerization and a method for producing such a catalyst. A particular aspect of the present invention relates to a method for producing linear copolymers of ethylene and alpha-olefins of low density (LLDPE), and medium density, (MDPE).

20 The resins produced in accordance with the invention contain a polymer component with a relatively very high molecular weight, and their MWDs are multimodal. Blown film manufactured from these polymers exhibits excellent impact and tear properties. Furthermore, the resins can be processed
25 into film by high stalk extrusion techniques.

All commercial polyethylene resins used in high-stalk extrusion equipment have a relatively broad MWD as indicated by MFR values of 80 to 200. Although resins with relatively broad MWD exhibit good processability on high-stalk extrusion
30 equipment, their film toughness properties, such as tear strength, are relatively poor.

In contrast, polyethylene resins with a relatively narrow MWD are not suited for high-stalk film extrusion equipment. We found, however, that even polyethylene resins with a

relatively narrow MWD can be processed with such equipment if the resins contain a significant fraction of polymer molecules with very high molecular weights. Moreover, such resins exhibit excellent film properties such as impact strength and tear resistance.

One of the measures of MWD of a LLDPE or MDPE resin is its melt flow ratio (MFR), which is the ratio of the high-load melt index (HLMI or I_{21}) to the melt index (MI or I_2) for a given resin: $MFR = I_{21}/I_2$. The MFR value is an approximate indication of MWD of a polymer: the higher the MFR value, the broader the MWD. Common polyethylene resins for film applications usually have relatively low MFR values, e.g., of 15 to 30.

It is an object of the present invention to provide a high-activity catalyst for copolymerization of ethylene and alpha-olefins yielding products with a multimodal, relatively narrow MWD as indicated by MFR values in the 28 to 70 range. It is an additional object of the present invention to provide a catalytic process for copolymerizing ethylene with alpha-olefins which yields products with a bimodal MWD at high productivity.

A supported alpha-olefin polymerization catalyst composition of this invention is prepared in a multi-step process.

The process for catalyst production comprises

(i) providing a slurry in a non-polar solvent of a solid porous inorganic support having reactive hydroxyl groups; (ii) impregnating said support having hydroxyl groups, with $RMgR'$ compound, to form an intermediate, which intermediate has a Mg:hydroxyl group ratio of greater than 1,

wherein each of said R and R' is an alkyl group of 1 to 12 carbon atoms and is the same or different;

(iii) treating the intermediate of step (ii) with a halogen containing reagent to form an intermediate of step (iii); (iv) treating the intermediate of step (iii) with $TiCl_4$ to form a catalyst precursor which has a Ti/Mg ratio of

greater than 0.5; (v) combining the catalyst precursor with a dialkylaluminum halide compound,

wherein said halogen containing reagent is effective in increasing the activity of a catalyst consisting of said support, said RMgR', said TiCl₄, and said aluminum.

The invention is also directed to copolymerization processes of ethylene and alpha-olefins conducted in the presence of the catalyst composition of this invention.

Figure 1 is a GPC chromatogram of a resin produced with a catalyst comprising product precursor of Example 1.

Figure 2 is a GPC chromatogram of a resin produced with a catalyst comprising product precursor of Example 2.

Figure 3 is a GPC chromatogram of a resin produced with a catalyst comprising product precursor of Example 3.

Figure 4 is a GPC chromatogram of a resin produced with a catalyst comprising product precursor of Example 4.

Figure 5 is a GPC chromatogram of a resin produced with a catalyst comprising product precursor of Example 5.

Figure 6 is a GPC chromatogram of a resin produced with the catalyst product of Example 6.

Figure 7 is a GPC chromatogram of a LLDPE resin produced with a catalyst in which trimethylaluminum (TMA) was used as a substitute for DMAC.

Figure 8 is a GPC chromatogram of a LLDPE resin produced with a catalyst in which triethylaluminum (TEAL) was used as a substitute for DMAC in the catalyst.

The catalysts herein exhibit unique catalytic effects in olefin polymerization. In polyolefin polymerizations and copolymerizations, the catalysts produce bimodal and trimodal molecular weight distribution products, in a single reactor. Bimodal molecular weight distribution means herein that the resin produced by the catalysts of the invention contain a first relatively lower molecular weight component and a second component of relatively higher molecular weight than said first component.

Trimodal molecular weight distribution, as used herein, means that the resin produced by the catalysts of the invention contains three components which differ from each other in molecular weight, a first relatively low molecular weight component and a second component of relatively intermediate molecular weight than said first component and the third component, which has the highest molecular weight of said three components. The amount of high molecular weight component in the bimodal or trimodal product, in weight percent, can range from 5 to 50%.

The resins so produced exhibit MFR I21/I2.16 of 25 to 80, preferably 30 to 75, and most preferably, 35 to 70.

The resins, fabricated into films exhibit superior dart impact properties and machine direction (MD) tear properties. Dart impact is measured by ASTM D-1709, Method A: with a 38.1 mm dart, and a drop height of 0.66 meters. MD tear is measured by ASTM D-1922 and reported as grams [g/1 mil (thickness)]. For example, the films of the invention exhibit dart drop in the range of 50 g to 1500 g, preferably from 100 g to greater than 800 g and most preferably >400 grams to >800 grams of test dart for a 1.0 mil thick film. A dart impact value of >800 grams means that the polymer film did not puncture more than 50% of the times that a dart of 800 gram mass was dropped onto the film. Accordingly, preferred products exhibit dart drop values in the range of 400 to 1500 and preferably 800 to 1500. Conventional LLDPE, at .918 density, exhibits a dart drop of 80 to 90 and MD tear of 100. Accordingly, resins produced with catalysts of the invention exhibit film toughness properties which combine both dart impact strength and high machine direction (MD) tear strength. Thus the films exhibit 20 to 100% improvement in dart drop over the films prepared with previously known catalysts and yet maintain MD tear values greater than 100 grams.

In addition to affording products of polymerization which exhibit unexpected properties compared to those produced from conventional Ziegler catalysts, the products of polymerization

can be used in high stalk extrusion processes. This is entirely unexpected for products produced by the catalysts of the invention which exhibit densities less than 0.94 and less than 0.93, as the LLDPE of conventional catalysts cannot be
5 run on high stalk extrusion.

The unique catalyst compositions of the invention comprise a precursor composition and a dialkylaluminum halide, such as DMAC (dimethylaluminum chloride) as an activator therefor.

10 Precursors produced according to the present invention are described below in terms of the manner in which they are made.

The carrier material is a solid, particulate, porous, preferably inorganic material. These carrier materials
15 include inorganic materials, such as oxides of silicon and/or aluminum. The carrier material is used in the form of a dry powder having an average particle size of from 1 micron to 250 microns, preferably from 10 microns to 150 microns. The carrier material is also porous and has a surface area of at
20 least 3 square meters per gram (m^2/gm), and preferably at least 50 m^2/gm . The carrier material should be dry, that is, free of absorbed water. Drying of the carrier material can be effected by heating at 100° to 1000°C, preferably at 600°C. When the carrier is silica, it is heated to at least 200°C,
25 preferably 200° to 850°C and most preferably at 600°C. The carrier material must have at least some active hydroxyl (OH) groups to produce the catalyst composition of this invention.

In the most preferred embodiment, the carrier is silica which, prior to the use thereof in the first catalyst
30 synthesis step, has been dehydrated by fluidizing it with dry nitrogen or dry air and heating at 600°C for 4 to 16 hours to achieve a surface hydroxyl group concentration of 0.7 millimoles per gram. The silica of the most preferred embodiment is a high surface area, amorphous silica (surface
35 area = 300 m^2/gm ; pore volume of 1.65 cm^3/gm), and it is a material marketed under the tradenames of Davison 952 or

Davison 955 by the Davison Chemical Division of W.R. Grace and Company. The silica is in the form of spherical particles, e.g., as obtained by a spray-drying process.

5 The carrier material is slurried in a non-polar solvent and the resulting slurry is contacted with at least one organomagnesium compound. The slurry of the carrier material in the solvent is prepared by introducing the carrier into the solvent, preferably while stirring, and heating the mixture to 25° to 100°C, preferably to 40° to 60°C. The slurry is then
10 contacted with the aforementioned organomagnesium compound, while the heating is continued at the aforementioned temperature.

The organomagnesium compound has the empirical formula



15 where R and R' are the same or different C₂-C₁₂ alkyl groups, preferably C₄-C₁₀ alkyl groups, more preferably C₄-C₈ alkyl groups, and most preferably both R and R' are butyl groups, and m and n are each 0, 1 or 2, providing that m + n is equal to the valence of Mg.

20 The most preferred halogen containing reagent is CCl₄, carbon tetrachloride.

Suitable non-polar solvents are materials in which all of the reactants used herein, i.e., the organomagnesium compound, the halogen containing reagent and the transition metal
25 compound, are at least partially soluble and which are liquids at reaction temperatures. Preferred non-polar solvents are alkanes, such as isopentane, hexane, n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such
30 as benzene and ethylbenzene, may also be employed. The most preferred non-polar solvent is isopentane. Prior to use, the non-polar solvent should be purified, such as by percolation through silica gel and/or molecular sieves, to remove traces

of water, oxygen, polar compounds, and other materials capable of adversely affecting catalyst activity.

In the most preferred embodiment of the synthesis of this catalyst it is important to add only such an amount of the organomagnesium compound that will be deposited - physically or chemically - onto the support since any excess of the organomagnesium compound in the solution may react with other synthesis chemicals and precipitate outside of the support. The carrier drying temperature affects the number of sites on the carrier available for the organomagnesium compound - the higher the drying temperature the lower the number of sites. Thus, the exact molar ratio of the organomagnesium compound to the hydroxyl groups will vary and must be determined on a case-by-case basis to assure that only so much of the organomagnesium compound is added to the solution as will be deposited onto the support without leaving any excess of the organomagnesium compound in the solution. Furthermore, it is believed that the molar amount of the organomagnesium compound deposited onto the support is greater than the molar content of the hydroxyl groups on the support. Thus, the molar ratios given below are intended only as an approximate guideline and the exact amount of the organomagnesium compound in this embodiment must be controlled by the functional limitation discussed above, i.e., it must not be greater than that which can be deposited onto the support. If greater than that amount is added to the solvent, the excess may react with other compounds involved in the synthesis, thereby forming a precipitate outside of the support which is detrimental in the synthesis of our catalyst and is avoided. The amount of the organomagnesium compound which is not greater than that deposited onto the support can be determined in any conventional manner, e.g., by adding the organomagnesium compound to the slurry of the carrier in the solvent, while stirring the slurry, until the organomagnesium compound is detected as a solution in the solvent.

For example, for the silica carrier heated at 600°C, the amount of the organomagnesium compound added to the slurry is such that the molar ratio of Mg to the hydroxyl groups (OH) on the solid carrier is 1:1 to 3:1, preferably 1.1:1 to 2:1, more preferably 1.2:1 to 1.8:1 and most preferably 1.4:1. The Mg loading on a silica support may be 0.7 to 1.3 mmole Mg/gram silica. The organomagnesium compound dissolves in the non-polar solvent to form a solution from which the organomagnesium compound is deposited onto the carrier.

It is also possible to add such an amount of the organomagnesium compound which is in excess of that which will be deposited onto the support, and then remove, e.g., by filtration and washing, any excess of the organomagnesium compound. However, this alternative is less desirable than the most preferred embodiment described above.

The slurry containing the organomagnesium contacted support is treated with the halogen containing reagent, in the absence of a transition metal compound. Reaction is usually detected by a color change. The halogen containing reagent is selected from the group consisting of carbon tetrachloride and trichloroethane; and is most preferably carbon tetrachloride. The molar ratio of halogen containing reagent to organomagnesium can range from 0.3 to 3; more preferably, the halogen reagent/Mg ratio is 0.46 to 2.57 and most preferably 1.32. The carbon tetrachloride loading may range from 0.6 to 1.8 mmoles/gram silica. The temperature of the treatment with the halogen containing reagent is 20° to 60°C. The effect of this treatment step is to increase the activity and flow index response of the catalyst.

The slurry is contacted with at least one transition metal compound soluble in the non-polar solvent. This synthesis step is conducted at 25° to 65°C, preferably at 30° to 60°C, and most preferably at 40° to 55°C. In a preferred embodiment, the amount of the transition metal compound added is not greater than that which can be deposited onto the carrier. By way of illustration, it is noted that the

titanium loading on silica can range from 0.7 to 1.3 mmole Ti/gram of silica, and preferably is 1.0 mmole Ti/gram silica. The exact molar ratio of Mg to the transition metal and of the transition metal to the hydroxyl groups of the carrier will
5 therefore vary (depending, e.g., on the carrier drying temperature) and must be determined on a case-by-case basis. For example, for the silica carrier heated at 200° to 850°C, the amount of the transition metal compound is such that the molar ratio of the transition metal, derived from the
10 transition metal compound, to the hydroxyl groups of the carrier is 1 to 2.0, preferably 1.2 to 1.8. The amount of the transition metal compound is also such that the molar ratio of Mg to the transition metal is 0.5 to 2.0, preferably 0.7 to 1.3 and most preferably 1.0.

15 Suitable transition metal compounds used herein are compounds of metals of Groups IVA, VA, VIA or VIII of the Periodic Chart of the Elements, as published by the Fisher Scientific Company, Catalog No. 5-702-10, 1978, providing that such compounds are soluble in the non-polar solvents. Non-
20 limiting examples of such compounds are titanium and vanadium halides, e.g., titanium tetrachloride (TiCl_4), vanadium tetrachloride (VCl_4), vanadium oxytrichloride (VOCl_3), titanium and vanadium alkoxides, wherein the alkoxide moiety has a branched or unbranched alkyl radical of 1 to 20 carbon atoms,
25 preferably 1 to 6 carbon atoms. The preferred transition metal compounds are titanium compounds, preferably tetravalent titanium compounds. The most preferred titanium compound is titanium tetrachloride.

Mixtures of such transition metal compounds may also be
30 used and generally no restrictions are imposed on the transition metal compounds which may be included. Any transition metal compound that may be used alone may also be used in conjunction with other transition metal compounds.

After synthesis of the precursor is completed, the non-
35 polar solvent is slowly removed, e.g., by distillation or evaporation. The temperature at which the non-polar solvent

is removed from the synthesis mixture can affect the productivity of the resulting catalyst compound. Lower solvent removal temperatures produce catalyst compositions which are more active than those produced with higher solvent removal temperatures. For this reason, it is preferred to
5 remove the non-polar solvent at 40° to 65°C, preferably at 45° to 55°C and most preferably at 55°C by drying, distillation or evaporation or any other conventional means. Excess amounts of halogen containing reagent can be removed simultaneously
10 with the non-polar solvent(s). The excess halogen containing reagent may also be removed by filtration and washing the silica prior to addition of the transition metal compound. The most preferred precursor composition per gram silica comprises 1.00 mmole dibutylmagnesium (DBM); 1.32 mmole carbon
15 tetrachloride and 1.00 mmole TiCl_4 .

The resulting free-flowing powder, referred to herein as a catalyst precursor, is combined with the activator. It was found that the combination of the precursor of this invention with the activator produces an alpha-olefin polymerization
20 catalyst composition having very high activity.

The activator used herein is a dialkylaluminum halide, e.g., DMAC (di-methylaluminum chloride). The activator is used in an amount which is at least effective to promote the polymerization activity of the solid catalyst component of
25 this invention. The amount of the activator is sufficient to give an Al:Ti molar ratio of 15:1 to 1000:1, preferably 20:1 to 300:1, and most preferably 25:1 to 100:1.

Without wishing to be bound by any theory of operability, it is believed that the catalyst composition of this invention
30 is produced by chemically impregnating the support with catalyst components sequentially added to the slurry of the carrier in the non-polar solvent. Therefore, all of the catalyst synthesis chemical ingredients must be soluble in the non-polar solvent used in the synthesis. The order of
35 addition of the reagents may also be important since the catalyst synthesis procedure is predicated on the chemical

reaction between the chemical ingredients sequentially added to the non-polar solvent (a liquid) and the solid carrier material or a catalyst intermediate supported by such a material (a solid). Thus, the reaction is a solid-liquid
5 reaction. For example, the catalyst synthesis procedure must be conducted in such a manner as to avoid the reaction of two or more reagents in the non-polar solvent to form a reaction product insoluble in the non-polar solvent outside of the pores of the solid catalyst support. Such an insoluble
10 reaction product would be incapable of reacting with the carrier or the catalyst intermediate and therefore would not be incorporated onto the solid support of the catalyst composition.

The catalyst precursors of the present invention are
15 prepared in the substantial absence of water, oxygen, and other catalyst poisons. Such catalyst poisons can be excluded during the catalyst preparation steps by any well known methods, e.g., by carrying out the preparation under an atmosphere of nitrogen, argon or other inert gas.
20 Purification of the non-polar solvent employed in the catalyst is also helpful in this regard.

The catalyst may be activated in situ by adding the activator and catalyst separately to the polymerization medium. It is also possible to combine the catalyst and the
25 activator before the introduction thereof into the polymerization medium, e.g., for up to 2 hours prior to the introduction thereof into the polymerization medium at a temperature of from -40° to 100°C.

The DMAC activator is employed in an amount which is at
30 least effective to promote the polymerization activity of the solid component of the precursor composition.

The catalyst may be activated in a polymerization reactor by adding the activator and the catalyst precursor separately to the polymerization medium. It is also possible to combine
35 the catalyst precursor and the activator before the introduction thereof into the polymerization medium, e.g., for

up to 2 hours prior to the introduction thereof into the polymerization medium, at a temperature of -40° to 100°C .

The amount of the activator is conventionally expressed in terms of the number of moles of the activator per gram atom of titanium in the catalyst composition, and varies from 5 to 300, preferably 20 to 200 moles of DMAC per gram atom of titanium.

Ethylene and its mixtures with alpha-olefins are polymerized with the catalysts prepared according to the present invention by any suitable process. Such processes include polymerizations carried out in suspension, in solution or in the gas phase. Gas phase polymerization reactions are preferred, e.g., those taking place in stirred bed reactors and, especially, fluidized bed reactors.

A particularly desirable method for producing polyethylene copolymers according to the present invention is in a fluid bed reactor. Such a reactor and method for operating the same are described by Nowlin et al, U.S. Patent No. 4,481,301, the entire contents of which is incorporated herein by reference.

The molecular weight of the polymer may be controlled in a known manner, e.g., by using hydrogen. With the catalysts produced according to the present invention, molecular weight may be suitably controlled with hydrogen when the polymerization is carried out at relatively low temperatures, e.g., from 70° to 105°C . The molecular weight control is evidenced by an increase in the melt index (I_2) of the polymer when the molar ratio of hydrogen to ethylene in the reactor is increased.

The molecular weight distribution of the polymers prepared in the presence of the catalysts of the present invention, as expressed by the melt flow ratio (MFR) values, varies from 26 to 70 for LLDPE products having a density of 0.92 to 0.94 gms/cc, and I_2 of 0.1 to 0.7. As is known to those skilled in the art, such MFR values are indicative of a relatively narrow molecular weight distribution, thereby

rendering the polymers especially suitable for low density film applications since the products exhibit less molecular orientation in high-speed film blowing processes, and therefore have greater film strength.

5 The physical and mechanical properties of the films made from the resins polymerized with the catalysts of this invention are better than those of the resins polymerized with trialkyl aluminum compounds such as triethyl aluminum.

10 The productivity of the catalysts prepared according to the present invention is at least 1,000, and can be as much as 5,000, grams of polymer per gram of catalyst precursor per 100 psi of ethylene partial pressure.

15 The polyethylene polymers prepared in accordance with the present invention may be homopolymers of ethylene or copolymers of ethylene with one or more C_3 - C_{10} alpha-olefins. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/propylene copolymers, ethylene/1-butene copolymers, ethylene/1-hexene
20 copolymers, ethylene/4-methyl-1-pentene copolymers, ethylene/1-butene/1-hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers. The most preferred polymers are copolymers of ethylene with 1-hexene, 1-butene or 4-methyl-1-pentene.

25 The ethylene copolymers produced in accordance with the present invention preferably contain at least 80% by weight of ethylene units, and most preferably contain 90% of ethylene units.

30 The following Examples further illustrate the essential features of the invention. However, it will be apparent to those skilled in the art that the specific reactants and reaction conditions used in the Examples do not limit the scope of the invention.

35 The properties of the polymers produced in the Examples were determined by the following test methods:

5	Density	ASTM D-1505 - A plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient column; reported as gms/cc.
	Melt Index (MI), I ₂	ASTM D-1238 - Condition E - Measured at 190°C - reported as grams per 10 minutes.
10	High Load Melt (HLMI), Index I ₂₁	ASTM D-1238 - Condition F - Measured at 10.5 times the weight used in the melt index test above.
	Melt Flow Ratio (MFR)= I ₂₁ /I ₂	
15	Comonomer Content	Comonomer contents of ethylene copolymers were measured by the infrared spectroscopic method, as described in the article of T. E. Nowlin, Y. V. Kissin and K. P. Wagner HIGH ACTIVITY ZIEGLER-NATTA CATALYST FOR THE PREPARATION OF ETHYLENE COPOLYMERS, Journal of Polymer Science: Part A: Polymer Chemistry, Volume 26, pages 755-764 (1988).
20	n-hexane Extractables	(FDA test used for polyethylene film intended for food contact applications). A 200 square inch sample of 1.5 mil gauge film is cut into strips measuring 1" x 6" and weighed to the nearest 0.1 mg. The strips are placed in a vessel and extracted with 300 ml of n-hexane at 50± °C for 2 hours. The extract is then decanted into tared culture dishes. After drying the extract in a vacuum desiccator the culture dish is weighed to the nearest 0.1 mg. The extractables, normalized with respect to the original sample weight, is then reported as the weight fraction of n-hexane extractables.
30		
	Dart Impact	ASTM D1709 Free Falling DART Method (F50)
35	Tear Strength	ASTM D-1922

EXAMPLES

Example 1

Catalyst (A): 3.04 grams of 955-600 silica was weighed into a 100 ml pear-flask, containing a magnetic stirring bar, followed by ca. 40 ml of dry heptane. The flask was placed into a 62°C oil bath. Next, 4.2 ml of dibutylmagnesium (0.736 mmol/ml) was added to the silica/heptane slurry. The contents of the flask were stirred for 45 minutes. Then, 2.8 ml of a

2.156 Molar solution of 1-butanol in heptane was added to the flask and the contents were stirred for 55 minutes. [Note: 1.0 mmol of Mg/g silica and 2.0 mmol of butanol/g silica, butanol/Mg molar ratio of 2.0 was used]. Finally, 3.3 ml of titanium tetrachloride (0.918 Molar solution in heptane) was added to the flask and stirring was continued for 45 minutes. Finally, the solvents were removed from the flask with a nitrogen purge and 3.8 grams of a white free-flowing powder were obtained.

10 Example 2

Catalyst (B): 3.04 grams of 955-600 silica was weighed into a 100 ml pear-flask, containing a magnetic stirring bar, followed by ca. 40 ml of dry heptane. The flask was placed into a 63°C oil bath. Next, 2.55 ml of dibutylmagnesium (0.754 mmol/ml) was added to the silica/heptane slurry. The contents of the flask were stirred for 90 minutes. Next, 2.55 ml of dibutylmagnesium (0.754 mmol/ml) was added to the silica/heptane slurry. The contents of the flask were stirred for 90 minutes. Next, 3.3 ml of titanium tetrachloride (0.918 Molar solution in heptane) was added to the flask and stirring was continued for 45 minutes. Finally, the solvents were removed from the flask with a nitrogen purge and 3.5 grams of a dark brown, free-flowing powder were obtained.

Example 3

25 Catalyst (C): 5.06 grams of 955-600 silica was weighed into a 300 ml pear-flask, containing a magnetic stirring bar, followed by ca. 75 ml of dry heptane. The flask was placed into a 55°C oil bath. Next, 6.88 ml of dibutylmagnesium (0.736 mmol/ml) was added to the silica/heptane slurry. The contents of the flask were stirred for 80 minutes. Then, 4.16 ml of a 1.606 Molar solution of carbon tetrachloride in heptane was added to the flask and the contents were stirred for 45 minutes. [Note: 1.0 mmol of Mg/g silica and 1.32 mmol of CCl₄/g silica was used]. Finally, 5.52 ml of titanium tetrachloride (0.918 Molar solution in heptane) was added to the flask and stirring was continued for 45 minutes. Finally,

the solvents were removed from the flask with a nitrogen purge and 5.59 grams of a light brown free-flowing powder were obtained.

Example 4

5 Catalyst (D): 207.1 grams of 955-600 silica was weighed into a four-neck, 3-liter round-bottom flask fitted with an overhead stirrer. The flask was placed into an oil bath at ca. 60°C and 1300 ml of dry heptane was added to the flask. Next, 282
10 ml of dibutylmagnesium (0.736 mmol/ml) was added to the silica/heptane slurry over a period of 5 minutes. Then, 25 ml of 1,1,1 trichloroethane was added to the flask in 40 seconds and the contents were stirred for 60 minutes. Next, 20.5 ml of titanium tetrachloride was added to the flask and stirring was continued for 60 minutes. Finally, the solvents were
15 removed from the flask with a nitrogen purge and 230 grams of a light brown free-flowing powder were obtained.

Example 5

Catalyst (E): 6.00 grams of 955-600 silica was weighed into a 300 ml pear-flask, containing a magnetic stirring bar,
20 followed by ca. 100 ml of dry heptane. The flask was placed into a 55°C oil bath. Next, 8.15 ml of dibutylmagnesium (0.736 mmol/ml) was added to the silica/heptane slurry. The contents of the flask were stirred for 62 minutes. Then, 0.88 ml of tetraethyl orthosilicate was added to the flask and the
25 contents were stirred for 128 minutes. Finally, 1.76 ml of titanium tetrachloride (3.41 Molar solution in heptane) was added to the flask and stirring was continued for 57 minutes. Finally, the solvents were removed from the flask with a nitrogen purge and 3.4 grams of a free-flowing powder were
30 obtained.

Example 6

Catalyst (F) A catalyst precursor was synthesized according to the teachings of Yamaguchi et al., U.S. Patent No. 3,989,881, and Karol et al., European Patent Application No.
35 84103441.6.

(a) Preparation of Precursor

In a 12 liter flask equipped with a mechanical stirrer were placed 41.8g (0.439 mol) of anhydrous $MgCl_2$ and 2.5 liters of tetrahydrofuran (THF). To this mixture, 29.0 (0.146 mol) of $TiCl_3$, 0.33 $AlCl_3$ powder were added over a 1/2 hour period. The mixture was then heated at 60°C for another 1/2 hour in order to completely dissolve all materials.

Separately, five hundred grams of silica were dehydrated by heating at a temperature of 600°C and slurried in 3 liters of isopentane. The slurry was pretreated with 186 ml of a 20% by weight solution of TEAL in hexane which was added to the stirred silica slurry over a 1/4 hour period. The resulting mixture was then dried under a nitrogen purge at 60°C over a period of 4 hours to provide a dry, free-flowing powder containing 5.5% by weight of the aluminum alkyl.

The pretreated silica was then added to the solution of the catalyst precursor prepared as above. The resulting slurry was stirred for 1/4 hour and then the solvent (THF) was dried under a nitrogen purge at 60°C over a period of 4 hours to provide free-flowing powder of the catalyst precursor.

RESULTS AND DISCUSSION

Six different catalyst precursors of Examples 1-6 were evaluated with DMAC as cocatalyst in order to determine the effect of catalyst type on the amount of HMW component in the polymer. The laboratory slurry polymerization data is summarized in Table I. Typical slurry polymerization conditions in these experiments, as described for Catalyst D were as follows: A 1.6-liter stainless steel autoclave, at 53°C, was filled with 0.750 liters of dry heptane, 0.120 liters of dry 1-hexene and 3.0 mmol of dimethylaluminum chloride (DMAC) while under a slow nitrogen purge. The reactor was closed, the stirring rate was set at 900 rpm, the internal temperature was increased to 85°C, and the internal pressure was raised from 8.0 psi to 59 psi with hydrogen. Ethylene was introduced to maintain the pressure at 200 psig. Next, 0.0192 grams of Catalyst D was introduced into the

reactor with ethylene over-pressure and the temperature was continued for 60 minutes, then the ethylene supply was stopped and the reactor was allowed to cool to room temperature. A yield of 59.4 grams of polyethylene was collected. Flow index (HLMI) of this polymer was 8.67 and the Melt Flow Ratio (HLMI/MI) was 38.0 and the polymer contained 1.40 mol.% 1-hexene. The GPC chromatograms of the polymer prepared with each type of catalyst are illustrated in Figures 1-6.

TABLE I

Laboratory Slurry Polymerization Data

Catalyst*	Activity g/g/h	FI 21	MFR I ₂₁ /I ₂	1-Hexene mol%	HMW Component (wt%)	GPC Figure Number
A	2130	7.0	33.1	1.25	10.8	Figure 1
B	1250	10.6	52.2	1.35	13.4	Figure 2
C	2609	8.6	38.8	1.45	12.8	Figure 3
D	3080	8.7	38.0	1.40	10.8	Figure 4
E	1570	8.1	33.5	1.70	9.2	Figure 5
F	2390	12.8	28.9	1.15	7.2	Figure 6

*DMAC as activator

Each of the five catalysts A-E yielded a larger HMW-component than Catalyst F in both slurry and gas phase reactors. Catalyst F provided 7.2 wt.% of HMW component under slurry polymerization conditions while the five catalysts gave 9.2-13.4 wt.% of the HMW component in slurry.

Table II summarizes some gas phase fluid bed pilot plant product data for Catalyst F, Catalyst E and Catalyst C catalysts.

TABLE II
Pilot Plant Polymerization Data

	<u>Catalyst *</u>	<u>HME Component</u> <u>(wt.%)</u>	<u>Bubble</u> <u>Stability</u>
5	C	16.6	Excellent
	E	12.7	Good
	F	8.3	Poor

* DMAC as activator

10 This data show that Catalyst C gave a polymer with the largest amount (16.6 wt.%) HMW component while Catalyst E and Catalyst F produced 12.7 wt.% and 8.3 wt.% HMW component, respectively.

15 Four catalysts, catalysts A, B, C, E, gave a substantial amount of a LMW component in slurry polymerizations. In a slurry reactor, Catalyst D and Catalyst F did not produce much of a LMW component. Figures 1-6 illustrate the GPC chromatograms for each catalyst operated in a slurry reactor.

20 Catalysts C, E and F have been evaluated in the fluidized-bed pilot plant and the GPC chromatogram of the resins produced with these catalysts did not contain a distinct LMW component. From this data it is inferred that there is a process effect on the polymer composition under the polymerization conditions that we used. In slurry, resins produced with these catalysts possess a trimodal MWD; however, 25 the same catalysts produced resin in the pilot plant in which the LMW component was substantially absent.

The relative bubble stability of resins produced with DMAC cocatalyst in combination with precursors of Examples 3, 5 and 6 are described in the following Table.

1.0 mil film properties (Alpine)
4:1 BUR, 120 lbs/hr, 27" Stalk height

Commercial		Relatively Narrow MWD MFR 29-65				Commercial	
Phillips Marlex 12252		Catalyst of U.S. Patent No. 5,238,345		Example 6 Precursor*		OnyChem L5003	
		Example 5 Precursor	Example 3 Precursor	Example 6 Precursor*			
MI	0.26	0.2	0.1	0.3		0.05	
MFR	84	37	65	29		190	
Density, g/cc	0.922	0.926	0.923	0.922		0.949	
DDI, I ⁵⁰	670	>800	>800	>800		400	
MDT, g/mil	120	160	110	310		24	
Bubble Stability	Moderate	Moderate	Excellent	Poor		Good	

* - Could not draw down to 1.0 mil due to poor bubble stability

This is to cross-reference this application to its parent application; this application is a continuation in part application of copending Serial No. 08/008,854 filed January 5, 1993, which in turn is a Rule 62 continuation of Serial No. 07/712,298 filed June 10, 1991 (now abandoned). The following comparative examples 1-9 are from commonly assigned application S. N. 08/121,821.

Catalyst Precursor Preparation

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk techniques. Into a 200 ml Schlenk flask was placed 7.0 grams of Davison grade 955 silica, which was previously dried under a nitrogen purge at 600°C for 16 hours. Hexane (90 ml) was added to the silica. Dibutylmagnesium (7.0 mmol) was added to the stirred slurry at 50° to 55°C and stirring was continued for one hour. A halogen containing reagent (9.2 mmol) was added to the slurry (50° to 55°C) and stirring was continued for one hour. TiCl_4 (7.0 mmol) was added to the reaction medium (50° to 55°C) and stirring was continued for an additional hour. Hexane was then removed by distillation with a nitrogen purge at 50° to 55°C. Yield varied from 8.0-9.3 grams depending on the halogen containing reagent employed.

Polymerization

Ethylene/1-hexene copolymers were prepared with these catalysts under the same polymerization conditions. A typical example is shown below.

A 1.6 liter stainless steel autoclave under a slow nitrogen purge at 50°C was filled with 750 ml of dry hexane, 30 ml of dry 1-hexene, and 3.0 mmol of triethylaluminum. The reactor was closed, the stirring was increased to 900 rpm, and the internal temperature was increased to 85°C. The internal pressure was raised 12 psi with hydrogen. Ethylene was introduced to maintain the pressure at 120 psia. The internal temperature was decreased to 80°C, 20.0 mg of catalyst precursor was introduced into the reactor with ethylene over-pressure, and the internal temperature was increased and held

at 85°C. The polymerization was continued for 60 minutes, and then the ethylene supply was stopped and the reactor was allowed to cool to room temperature. The polyethylene was collected and air dried.

- 5 Given below are the catalyst productivities and polymer flow indexes and melt flow ratios (I_{21}/I_2). The catalysts were prepared according to the sequence.

DBM Silica ----->		Halogen Reagent ----->	TiCl ₄ ----->			
10 Ex. No.	Comparable Halogen Reagent	(1) Productivity	Co-Catalyst	Flow Index	H ₂ (2) (Psi)	MFR
	1 None (Control)	590	TEAL	2.4	12	70.1
	2 tin (IV) chloride	3830	TEAL	3.8	12	30.9
15	3 iodine	3240	TEAL	9.3	12	38.0
	4 iodine monochloride	3680	TEAL	6.0	12	38.3
	5 carbon tetrachloride	4660	TEAL	7.4	12	35.8
	6 carbon tetrachloride	3405	TEAL	11.7	14	34.3
20	7 carbon tetrachloride	4160	DIBAH	8.7	14	48.7
	8 carbon tetrachloride	3065	TEAL	416	76	30.5
	9 carbon tetrachloride	3100	DIBAH	720	76	36.9

(1) g polyethylene/g catalyst/hr/100 psi ethylene

(2) hydrogen pressure in polymerization reactor

- 25 Thus it is apparent that there has been provided, in accordance with the invention, a composition, that fully satisfies the objects, aims, and advantages set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many
- 30 alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims.

CLAIMS:

1. A catalyst composition for producing a product of bimodal or trimodal molecular weight distribution, comprising polymers and copolymers of ethylene, wherein the product is produced in a single reactor, wherein the product has a MFR which ranges from 28 to 70;

wherein product comprises at least two components and wherein 5 to 50 weight percent of the product is one of said two components and wherein said product has a second component, wherein the said one of said two components has molecular weight which is greater than that of the second component,

wherein the catalyst is formed by the steps comprising:

(i) providing a slurry of a non-polar solvent and a solid porous silica having -OH groups; (ii) impregnating said silica, with RMgR' , to form an intermediate (ii), wherein the -OH groups:Mg ratio is less than 1, wherein each of said R and R' is alkyl of 4 to 10 carbon atoms and is the same or different, wherein said RMgR' is soluble in said non-polar solvent; (iii) treating the intermediate (ii) with an amount of carbon tetrachloride, which amount is effective to provide a carbon tetrachloride: RMgR' molar ratio of 0.3 to 3, to form a step (iii) product; (iv) after (iii), treating the step (iii) product with TiCl_4 to form a catalyst precursor, wherein the -OH:Ti ratio is less than 1; and (v) combining the catalyst precursor with dimethylaluminum chloride as cocatalyst to activate the catalyst precursor.

2. The catalyst of Claim 1, wherein steps (ii) and (iv) are conducted at a temperature in the range of 40° to 60°C.

3. The catalyst composition of Claim 2, wherein R and R' are C₄-C₈ alkyl groups.

4. The catalyst composition of Claim 3, wherein R and R' are each butyl groups.

5 5. The catalyst composition of Claim 4, wherein the non-polar solvent is a hydrocarbon which is a liquid at ambient conditions.

6. The catalyst composition of Claim 2, wherein the amount of the TiCl₄ present in said step (iv) is such that the
10 molar ratio of Mg to Ti is 0.5 to 2.

7. The catalyst composition of Claim 6, wherein the amount of the TiCl₄ present in said step (iv) is such that the molar ratio of Mg to Ti is 0.75 to 1.5.

8. The catalyst composition of Claim 6, wherein the
15 amount of the organomagnesium compound used in said step (i) is such that the molar ratio of Mg:OH is 1:1 to 3:1.

9. The catalyst composition of Claim 7, wherein the amount of the organomagnesium compound used in said step (i) is such that the molar ratio of Mg:OH is 1.1:1 to 2:1.

20 10. The catalyst composition of Claim 8, wherein the amount of the organomagnesium compound used in said step (i) is such that the molar ratio of Mg:OH is 1.2:1 to 1.8:1.

11. The catalyst composition of Claim 10, wherein the
25 amount of the organomagnesium compound used in said step (i) is such that the molar ratio of Mg:OH is 1.4:1.

12. The catalyst composition of Claim 11, wherein the silica which, prior to contact thereof with the solvent in step (i), is heated at a temperature of at least 200°C.

13. The catalyst composition of Claim 12, wherein the
5 silica is heated at a temperature of 600°C.

14. The catalyst composition of Claim 13, wherein the silica has, after the heating, surface hydroxyl group concentration of 0.7 mmol/g, a surface area of 300 m²/gram and a pore volume of 1.65 m³/gram.

10 15. A catalyst composition for producing a product of bimodal or trimodal molecular weight distribution, comprising polymers and copolymers of ethylene, wherein the product is produced in a single reactor, wherein the product has a MFR which ranges from 28 to 70;
15 wherein product comprises at least two components and wherein 5 to 50 weight percent of the product is one of said two components and wherein said product has a second component, wherein the said one of said two components has molecular weight which is greater than that of the
20 second component,
wherein the catalyst is formed by the steps comprising:
(i) providing a slurry of a non-polar solvent and a solid porous silica having -OH groups;
(ii) impregnating said silica, with RMgR', to form an
25 intermediate (ii), wherein the -OH groups:Mg ratio is less than 1, wherein each of said R and R' is butyl, wherein said RMgR' is soluble in said non-polar solvent;
(iii) treating the intermediate (ii) with an amount of carbon tetrachloride, which amount is effective to
30 provide a carbon tetrachloride:RMgR' molar ratio of 0.3 to 3, to form a step (iii) product;

(iv) after (iii), treating the step (iii) product with TiCl_4 to form a catalyst precursor, wherein the $-\text{OH}:\text{Ti}$ ratio is less than 1; and

5 (v) combining the catalyst precursor with dimethylaluminum chloride as cocatalyst to activate the catalyst precursor.

16. The catalyst of Claim 1, wherein steps (ii) and (iv) are conducted at a temperature in the range of 40° to 60°C .

10 17. The catalyst composition of Claim 16, wherein the non-polar solvent is a hydrocarbon which is a liquid at ambient conditions.

18. The catalyst composition of Claim 16, wherein the amount of the TiCl_4 present in said step (iv) is such that the molar ratio of Mg to Ti is 0.5 to 2.

15 19. The catalyst composition of Claim 18, wherein the amount of the TiCl_4 present in said step (iv) is such that the molar ratio of Mg to Ti is 0.75 to 1.5.

20 20. The catalyst composition of Claim 18, wherein the amount of the organomagnesium compound used in said step (i) is such that the molar ratio of $\text{Mg}:\text{OH}$ is 1:1 to 3:1.

21. The catalyst composition of Claim 19, wherein the amount of the organomagnesium compound used in said step (i) is such that the molar ratio of $\text{Mg}:\text{OH}$ is 1.1:1 to 2:1.

25 22. The catalyst composition of Claim 20, wherein the amount of the organomagnesium compound used in said step (i) is such that the molar ratio of $\text{Mg}:\text{OH}$ is 1.2:1 to 1.8:1.

23. The catalyst composition of Claim 22, wherein the amount of the organomagnesium compound used in said step (i) is such that the molar ratio of Mg:OH is 1.4:1.

5 24. The catalyst composition of Claim 23, wherein the silica which, prior to contact thereof with the solvent in step (i), is heated at a temperature of at least 200°C.

25. The catalyst composition of Claim 23, wherein the silica is heated at a temperature of 600°C.

10 26. The catalyst composition of Claim 25, wherein the silica has, after the heating, surface hydroxyl group concentration of 0.7 mmoles/g, a surface area of 300 m²/gram and a pore volume of 1.65 m³/gram.

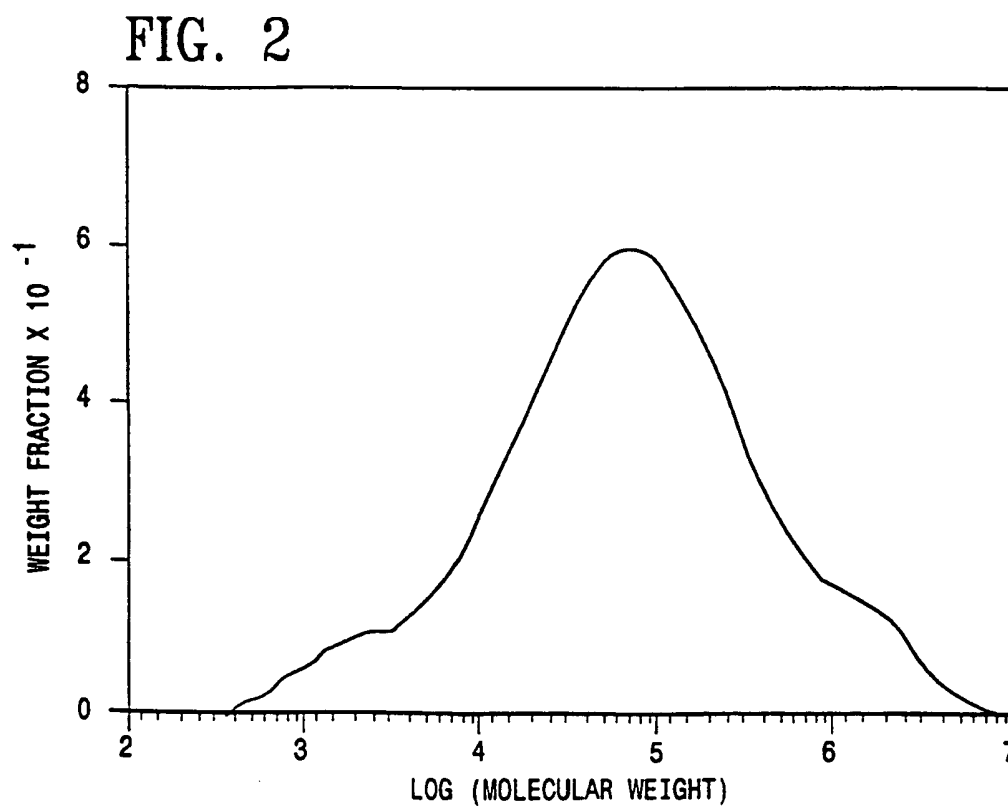
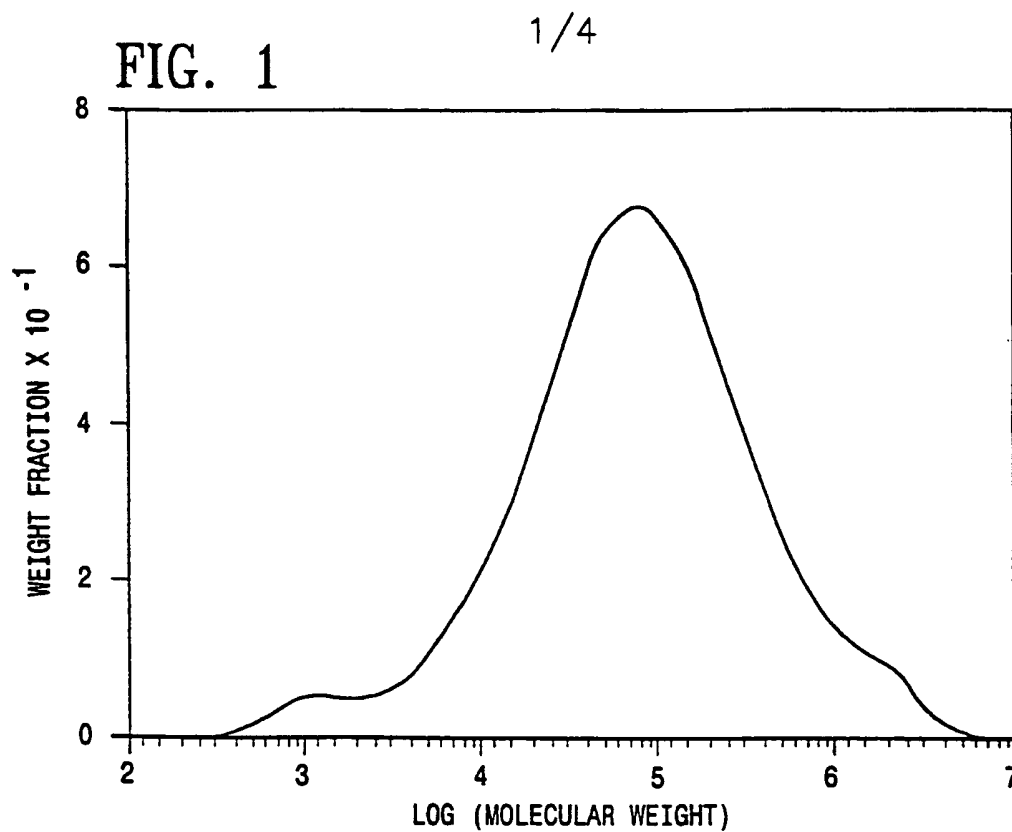


FIG. 3

2/4

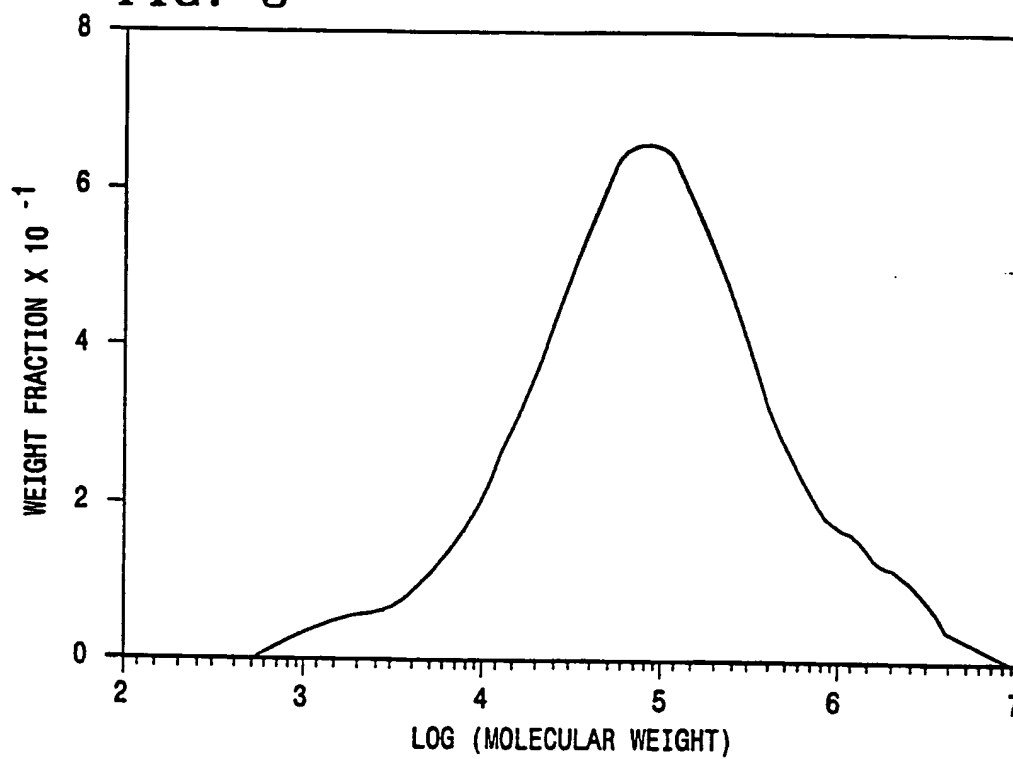


FIG. 4

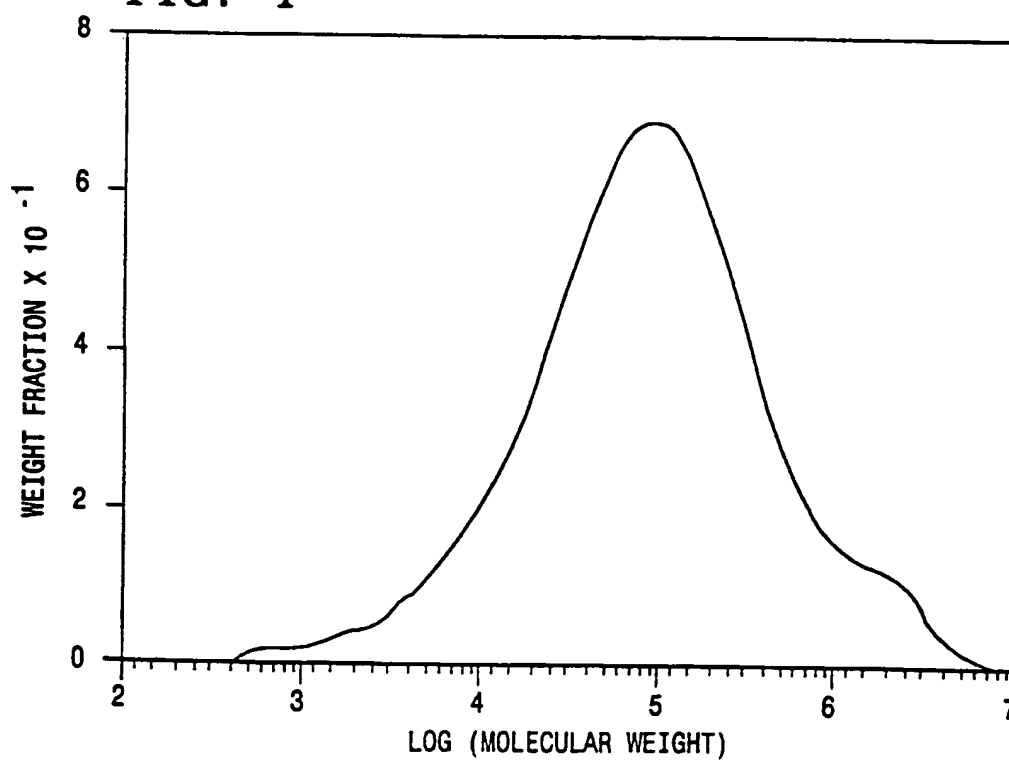


FIG. 5

3/4

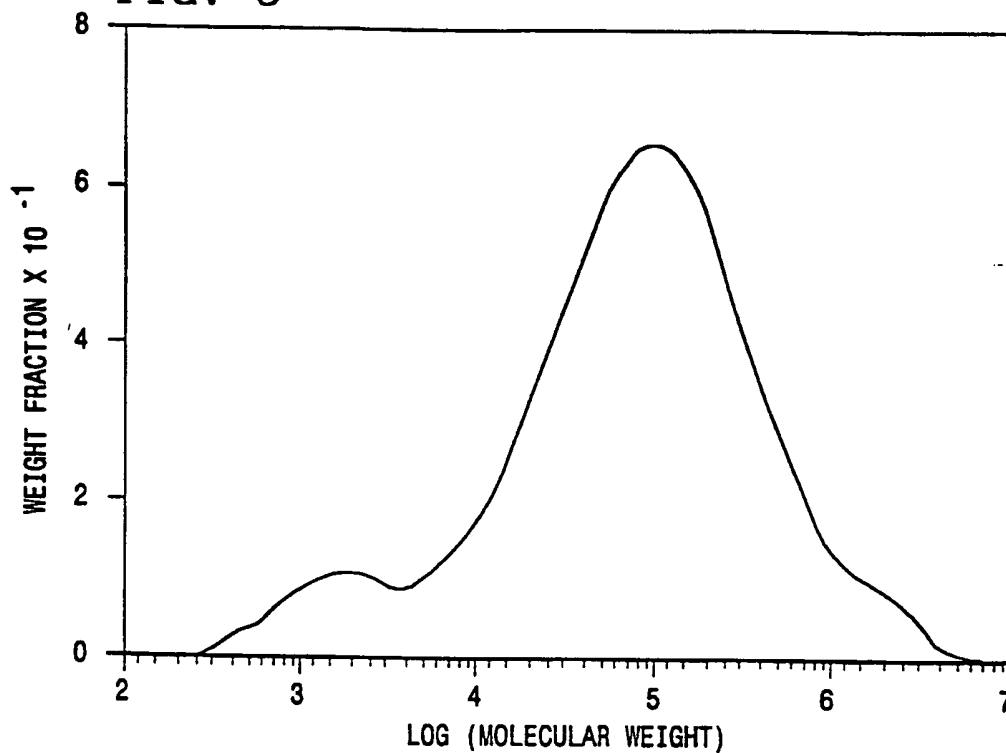
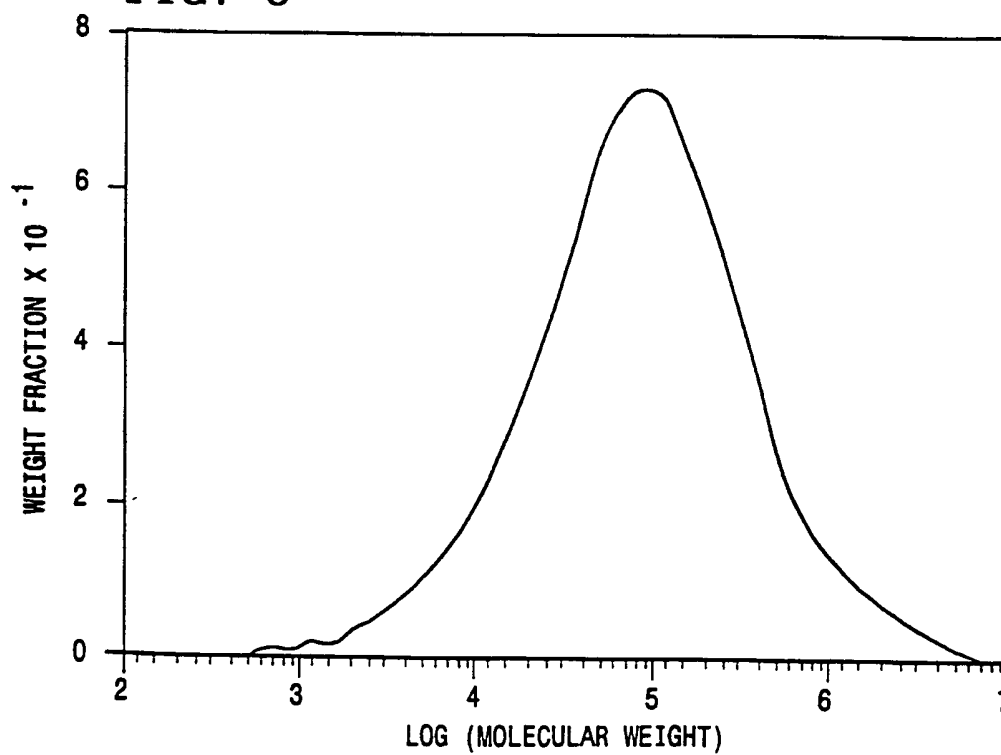
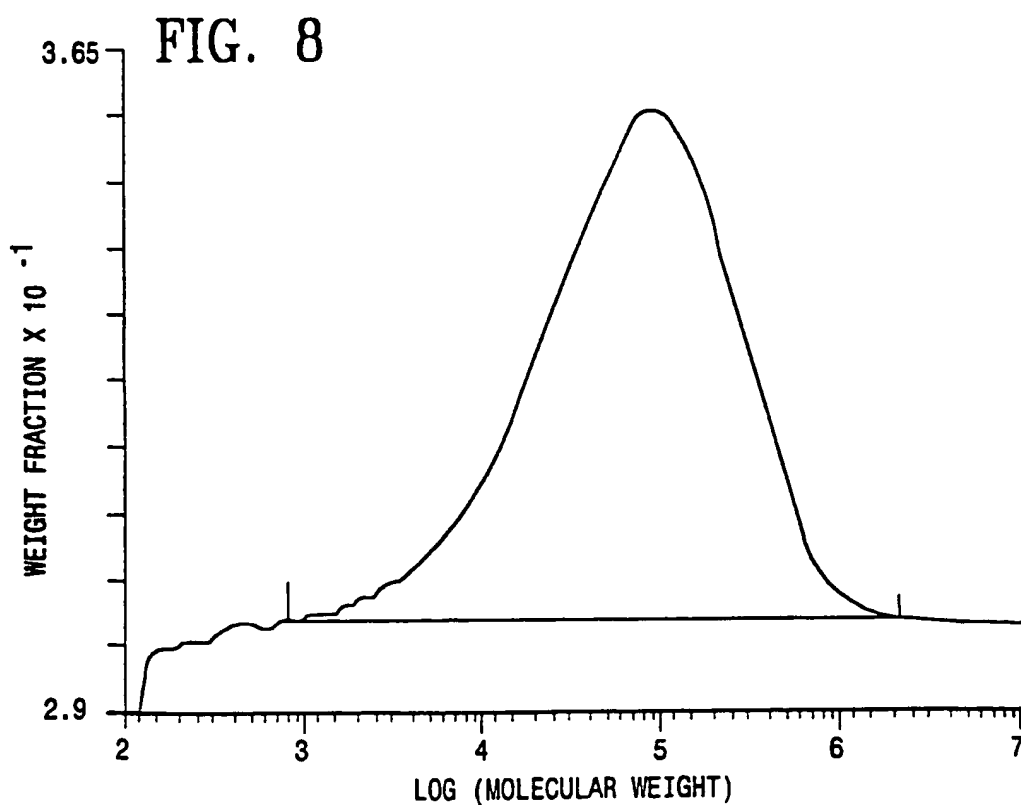
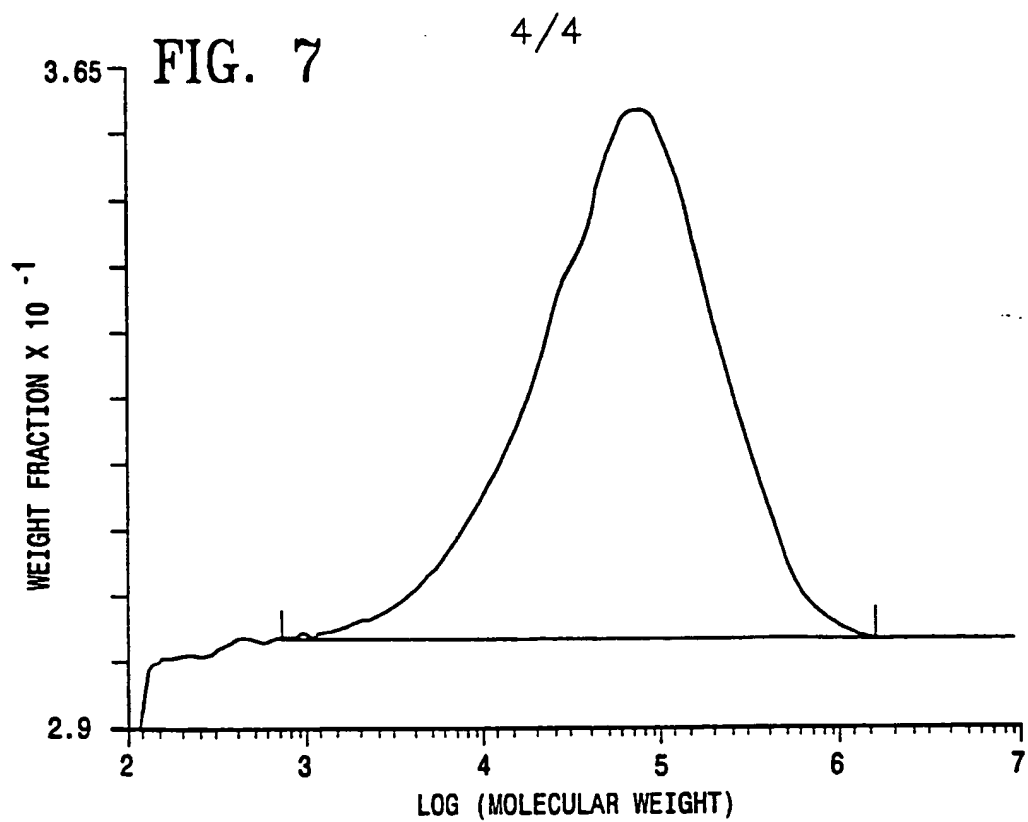


FIG. 6





INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/02561

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 31/00, 37/00; C08F 4/02, 4/60

US CL :502/104, 107, 115, 128

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/104, 107, 115, 128, 113, 114, 116, 120, 121

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 518 604 A (MINK et al) 16 December 1992, abstract; p. 2, lines 45-55; p. 3, line 47.	1-26
Y	US 4,362,648 A (DIETZ et al) 7 December 1982, col. 4, lines 58-61.	1-26
Y	EP 0 435 627 A (HAGGERTY et al) 3 July 1991, p. 6, line 57.	1-26
A	EP 0 435 557 A (HAGERTY et al) 3 July 1991, p. 7, lines 21-22.	1-26
A	US 4,301,029 A (CAUNT et al) 17 November 1981, col. 6, line 65 to col. 7, line 1.	1-26
A	US 4,173,547 A (GRAFF) 6 November 1979, col. 8, lines 18-27.	1-26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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